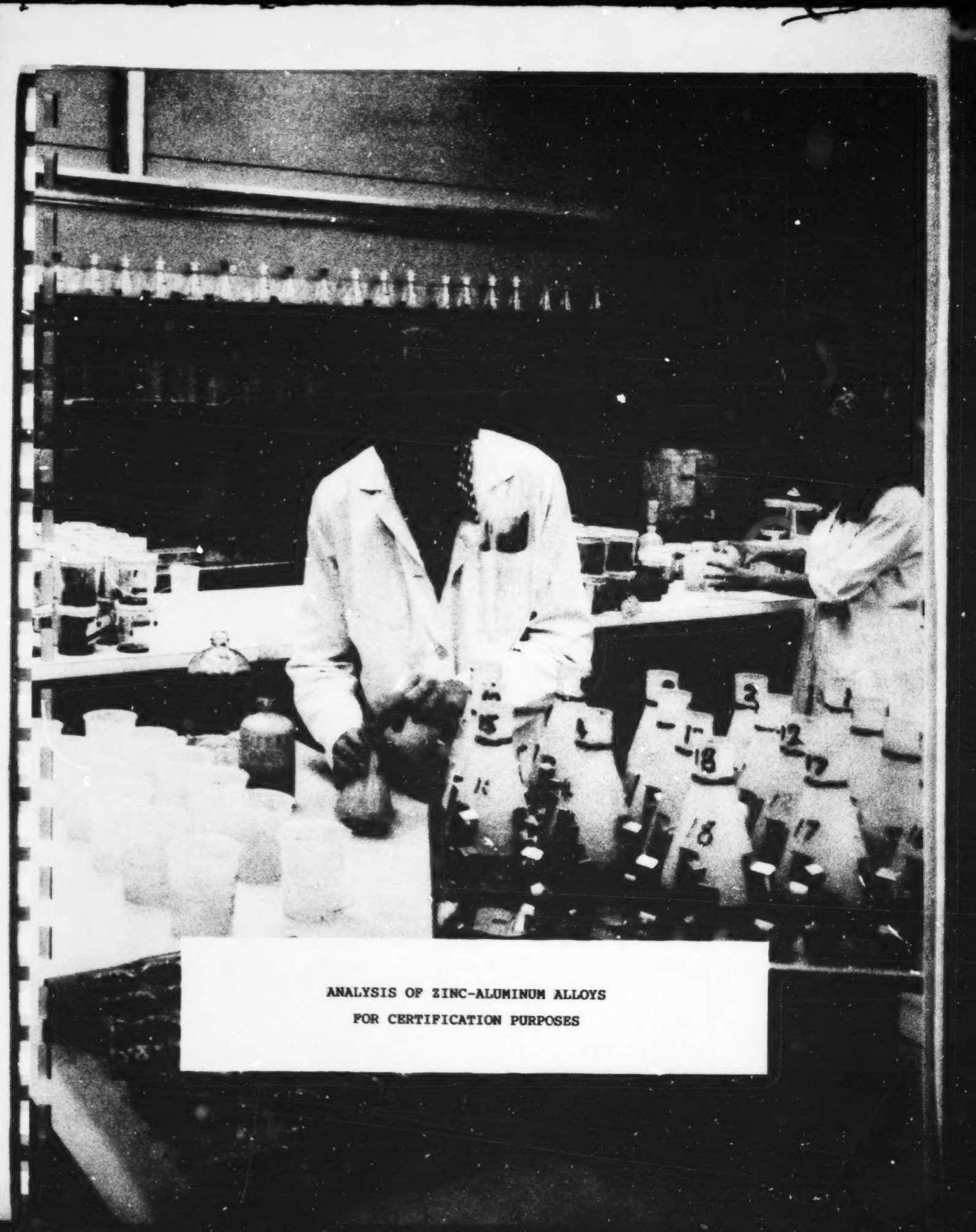

ANALYSIS OF ZINC-ALUMINUM ALLOYS

FOR CERTIFICATION PURPOSES

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EXECUTIVE SUMMARY

Seven zinc-aluminum alloy samples, designated "NAZ-1" through "NAZ-7" were analyzed to obtain recommended values for seven elements under the Canadian Certified Reference Materials Project.

Five separate subsamples of each sample were analyzed for the elements aluminum, cadmium, copper, iron, lead, magnesium, tin, using Inductively Coupled Argon Plasma Spectroscopy. Atomic Absorption Spectrophotometry was used to confirm the analyses for lead and cadmium.

In addition, Gravimetric Analysis was carried out on five separate subsamples of each sample for determination of the element aluminum.

RESUME EXECUTIF

Sept échantillons d'alliage de zinc et d'aluminium, appelés NAZ-1 à NAZ-7, ont été analysés pour obtenir les valeurs recommendées pour sept éléments dans le Projet Canadien de Référence de Matériaux Certifiés (Canadian Certified Reference Materials Project).

Cinq sous-échantillons indépendents de chaque échantillon ont été analysés pour les éléments d'aluminium, de cadmium, de cuivre, de fer, de plomb, de magnésium et d'étain, utilisant un spectroscope de plasma d'argon inductivement accouplé. Un spectrophotomètre d'absorption atomique a été utilisé pour confirmer les analyses de plomb et de cadmium.

Additionnellement, une Analyse Gravimétrique a été conduite sur cinq sous-échantillons indépendents de chaque échantillon pour déterminer l'élément d'aluminium.

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SAMPLE IDENTIFICATION

Seven glass bottles containing chip samples of alloy material were received by our laboratory. The bottles were labelled:

Zn/Al Alloy	NAZ-1	Bottle No. 88
Zn/Al Alloy	NAZ-2	Bottle No. 97
Zn/Al Alloy	NAZ-3	Bottle No. 73
Zn/Al Alloy	NAZ-4	Bottle No. 65
Zn/Al Alloy	NAZ-5	Bottle No. 129
Zn/Al Alloy	NAZ-6	Bottle No. 123
Zn/Al Alloy	NAZ-7	Bottle No. 3

METHOD OF ANALYSIS

The analytical scheme is summarized below:

- On five separate days, the seven submitted samples were digested in nitric acid, diluted to appropriate volume and analyzed for all seven elements of interest using Inductively Coupled Argon Plasma Spectroscopy (ICP) and/or Atomic Absorption Spectrophotometry (AA).

- On five separate days, the seven submitted samples were analyzed for aluminum using gravimetric analysis. The final aluminum oxide precipitates were examined for co-precipitated elements by digesting the precipitates and performing analysis by ICP. This data was used to apply corrections to the gravimetric analysis data.

1. Analysis of Alloy Samples by Plasma Spectroscopy and Atomic Absorption Spectrophotometry.

Prior to analysis, the sample material in each bottle was thoroughly mixed.

One gram samples, accurately weighed to 0.0001 gram using a Sartorius balance, were transferred to new, clean 400 ml beakers. Ten milliliters of BDH Analar concentrated nitric acid were added. The beakers were heated gently, if necessary, on a hot plate to effect complete digestion. In many cases, heating was not required.

The resulting solutions were diluted to 100.0 mls in volumetric flasks (designate "Solution A"). Ultrapure water obtained from a Culligan Reverse Osmosis Water Purification system was used for dilution. A further dilution was prepared by diluting 10.00 mls of the initial solution to 100.0 mls (designate solution "B"). Finally, a further ten-times dilution was carried out at the time of ICP Analysis using a Fisher Dilumat Diluter (designate "Solution C").

This analytical scheme (digestion of one gram samples and dilution to 100.0 mls) was performed to ensure lead analysis could be carried out at the levels expected.

Analysis was performed for the seven elements of interest (aluminum, cadmium, copper, iron, magnesium, lead and tin) using a Jarrell-Ash Model 975 Inductively Coupled Argon Plasma Spectrograph (ICP). The instrument was calibrated immediately before sample analysis using calibration standards prepared from pure metals or pure metal salts obtained from Johnson Matthey or from Spex Industries. Calibration standards for the elements under study were prepared at the level of 10.00 milligrams per liter. The ICP is equipped with a "Spectrum Shifter" background correction system and its onboard computer has the ability to correct for interelement direct spectral interferences. The ICP is equipped with an MAK all-glass high pressure nebulizer obtained from Sherritt Gordon Mines Ltd., Fort Saskatchewan Alta., and is assisted by a Gilson Minipuls peristaltic pump.

For the seven elements under study, the ICP Analytical wavelengths used were:

Aluminum	308.2 nm
Cadmium	226.5 nm
Copper	324.7 nm
Iron	259.9 nm
Magnesium	279.5 nm
Lead	220.3 nm
Tin	189.9 nm

ICP analysis was performed on the intermediate solution ("B") and on the dilute solution ("C").

Analysis using Flame Atomic Absorption Spectrophotometry (AA) was carried out for the elements cadmium and lead. Analysis was performed using a Varian Model 475 Atomic Absorption Spectrophotometer. Deuterium Background Correction was used for all measurements. The instrument was operated according to the manufacturer's recommendations.

Instrumental conditions were:

for Cadmium: 228.8 nm wavelength, 0.5 nm silt width, and oxidizing flame.

for Lead: 283.3 nm wavelength, 0.5 nm silt width, and oxidizing flame.

The instrument was calibrated using standard solutions prepared from pure lead nitrate and from pure cadmium metal.

Analysis was carried out on the concentrated solutions ("A").

Lead analysis was carried out by AA due to a significant spectral interference by aluminum on the 220.3 nm ICP lead analytical line. Cadmium AA analysis was used as a check on the ICP result since the cadmium levels in the analytical solution "B" were near or below the ICP detection limit for cadmium.

2. Gravimetric Analysis for Aluminum

Accurately weighed 0.25 gram samples (for samples NAZ-1 through NAZ-4) and 0.50 gram samples (for samples NAZ-5 through NAZ-7) were digested with 5 mls concentrated nitric acid, plus 15 mls concentrated hydrochloric acid. The solutions were cooled, and a small amount of ammonium chloride was added. Concentrated ammonium hydroxide was carefully added until a hydroxide precipitate formed; 5 mls excess was added. The solutions were boiled 10 minutes, and filtered through Whatman 541 Filter Paper. The precipitates were washed four times with two percent ammonium chloride solution. The precipitates were then carefully transferred back into their original beakers and 10 mls of concentrated hydrochloric acid were added. The precipitates were re-dissolved by boiling. The aluminum was re-precipitated as noted above (i.e. addition of ammonium chloride and ammonium hydroxide, boiling) and filtered using 541 paper. Any adhering precipitate was transferred using a rubber policeman. The precipitates were washed with two percent ammonium chloride solution and with water. Finally, the filter papers and contents were placed into tared porcelain crucibles, placed in a cold muffle furnace, and ignited to constant weight at 950°C.

The resulting Al_2O_3 precipitates were then digested with concentrated hydrochloric acid. The resulting solutions were analyzed by ICP for elements possibly contaminating the Al_2O_3 precipitate (namely iron, zinc, cadmium, tin, magnesium). If necessary, a correction factor was applied to the Al203 result to allow for co-precipitation by these elements. Finally, the percentage aluminum, as Al, was calculated.

QUALITY CONTROL

One Certified Aluminum Alloy Reference Standard was analyzed concurrently with each set of samples analyzed by ICP. The Reference Materials used were: British Chemical Standards B.C.S. No. 268, 5% Silicon Aluminum Alloy, and National Bureau of Standards, Standard Reference Material 87a, Silicon Aluminum Alloy. Results are tabulated in the "Results-Quality Control" section.

In addition, it should be noted that the ICP Analysis was carried out using a "general" or "all purpose" program. That is, the elemental array (30 elements) and calibration standards are used on a daily basis for the analysis of water, biological tissues, geological materials, and alloys. As it is our practice to analyze Certified Reference Materials with each set of samples, the analyses carried out for this project gained Quality Control support from other work in progress.

COMMENTS

It is our feeling that, with the exception of aluminum, the analysis was performed quickly, easily, and with a high degree of accuracy.

The results for aluminum indicate significant spread amongst each set of five results obtained by ICP and by Gravimetric Analysis. Agreement between ICP and Gravimetric results might not be termed "excellent".

It is now felt that our choice of the specific Gravimetric Procedure was not the best. Furthermore, this is not a "routine test" in our laboratory.

Unfortunately, time and scheduling restraints prohibit further investigations at this time.

RESULTS OF TESTING:

Sample Identification: NAZ-1

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav.	29.4%	29.5%	30.2%	30.8%	30.6%
		ICP	29.8%	30.5%	30.9%	30.6%	31.2%
Cadmium	Cd	ICP	L 15ppm	L 15ppm	L 15ppm	L 15ppm	L 15ppm
		AA	11ppm	12ppm	13ppm	12ppm	10ppm
Copper	Cu	ICP	1.39%	1.36%	1.35%	1.40%	1.40%
Iron	Fe	ICP	0.050%	0.050%	0.048%	0.051%	0.048%
Magnesium	Mg	ICP	0.018%	0.018%	0.018%	0.019%	0.018%
Lead	Pb	AA	29ppm	28ppm	28ppm	27ppm	27ppm
Tin	Sn	ICP	68ppm	66ppm	67ppm	70ppm	68ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CON'T)

Sample Identification: NAZ-2

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav	24.9	25.0	24.9	25.2	25.5
		ICP	25.0	25.7	26.4	25.6	26.6
Cadmium	Cd	ICP	48 ppm	48 ppm	49 ppm	51 ppm	50 ppm
		AA	51 ppm	53 ppm	53 ppm	51 ppm	49 ppm
Copper	Cu	ICP	2.72%	2.73%	2.74%	2.79%	2.75%
Iron	Fe	ICP	0.021%	0.021%	0.023%	0.023%	0.021%
Magnesium	Mg	ICP	0.026%	0.027%	0.027%	0.028%	0.027%
Lead	Pb	AA	73 ppm	77 ppm	75 ppm	77 ppm	71 ppm
Tin	Sn	ICP	45 ppm	42 ppm	38 ppm	42 ppm	40 ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CON'T)

Sample Identification: NAZ-3

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Alumimum	Al	Grav.	26.3%	27.5%	27.7%	27.2%	27.7%
		ICP	26.3%	27.7%	28.8%	28.2%	28.1%
Cadmium	Cd	ICP	66 ppm	67 ppm	67 ppm	70 ppm	71 ppm
		AA	67 ppm	68 ppm	68 ppm	67 ppm	65 ppm
Copper	Cu	ICP	1.83%	1.83%	1.85%	1.87%	1.88%
Iron	Fe	ICP	0.072%	0.071%	0.070%	0.075%	0.072%
Magnesium	Mg	ICP	41 ppm	47 ppm	46 ppm	51 ppm	49 ppm
Lead	Pb	AA	46 ppm	45 ppm	49 ppm	44 ppm	41 ppm
Tin	Sn	ICP	31 ppm	28 ppm	33 ppm	29 ppm	28 ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CONT'D)

Sample Identification: NAZ-4

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav.	27.5%	27.6%	27.7%	27.5%	27.5%
		ICP	27.8%	28.1%	28.3%	28.4%	28.7%
Cadmium	Cd	ICP	28 ppm	29 ppm	31 ppm	29 ppm	31 ppm
		AA	36 ppm	35 ppm	35 ppm	34 ppm	31 ppm
Copper	Cu	ICP	2.24%	2.18%	2.27%	2.35%	2.28%
Iron	Fe	ICP	0.027%	0.027%	0.029%	0.029%	0.028%
Magnesium	Mg	ICP	98 ppm	96 ppm	95 ppm	102 ppm	95 ppm
Lead	Pb	AA	109 ppm	102 ppm	108 ppm	102 ppm	95 ppm
Tin	Sn	ICP	90 ppm	90 ppm	80 ppm	91 ppm	97 ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CONT'D)

Sample Identification: NAZ-5

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav.	10.8%	11.2%	11.1%	11.1%	11.4%
		ICP	11.1%	11.8%	11.7%	11.6%	11.6%
Cadmium	Cd	ICP	95 ppm	98 ppm	99 ppm	106 ppm	105 ppm
		AA	92 ppm	94 ppm	95 ppm	95 ppm	93 ppm
Copper	Cu	ICP	0.95%	0.95%	0.94%	0.99%	0.97%
Iron	Fe	ICP	0.016%	0.017%	0.018%	0.017%	0.018%
Magnesium	Mg	ICP	0.019%	0.020%	0.019%	0.021%	0.020%
Lead	Pb	AA	11 ppm	12 ppm	12 ppm	12 ppm	10 ppm
Tin	Sn	ICP	L30 ppm	L30 ppm	L30 ppm	L30 ppm	L30 ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CONT'D)

Sample Identification: NAZ-6

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav.	7.73%	7.86%	7.70%	7.57%	7.91%
		ICP	7.83%	7.96%	8.21%	8.00%	8.32%
Cadmium	Cd	ICP	150 ppm	155 ppm	156 ppm	159 ppm	160 ppm
		AA	144 ppm	147 ppm	144 ppm	145 ppm	143 ppm
Copper	Cu	ICP	2.91%	2.86%	2.93%	3.01%	2.95%
Iron	Fe	ICP	0.021%	0.011%	0.011%	0.011%	0.010%
Magnesium	Mg	ICP	L 10 ppm	L 10 ppm	L 10 ppm	L 10 ppm	L 10 ppm
Lead	Pb	AA	790 ppm	815 ppm	795 ppm	803 ppm	800 ppm
Tin	Sn	ICP	52 ppm	45 ppm	50 ppm	55 ppm	50 ppm

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS OF TESTING: (CONT'D)

Sample Identification: NAZ-7

Element		Technique	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Aluminum	Al	Grav.	13.2%	13.6%	13.4%	13.4%	13.9%
		ICP	14.3%	14.2%	14.6%	14.3%	14.6%
Cadmium	Cd	ICP	L15 ppm	L15 ppm	L15 ppm	L15 ppm	L15 ppm
		AA	L10 ppm	L10 ppm	L10 ppm	L10 ppm	L10 ppm
Copper	Cu	ICP	0.20%	0.20%	0.20%	0.21%	0.20%
Iron	Fe	ICP	175 ppm	171 ppm	181 ppm	176 ppm	172 ppm
Magnesium	Mg	ICP	0.046%	0.048%	0.048%	0.048%	0.051%
Lead	Pb	AA	132 ppm	137 ppm	135 ppm	132 ppm	128 ppm
Tin	Sn	ICP	0.012%	0.011%	0.010%	0.011%	0.011%

ICP = Analysis by Inductively Coupled Argon Plasma Spectroscopy
AA = Analysis by Background Corrected Flame Atomic Absorption Spectrophotometry
Grav= Gravimetric Analysis
L = Less than
ppm = parts per million

RESULTS - QUALITY CONTROL

1. **National Bureau of Standards S.R.M. 87a, Silicon Aluminum Alloy**

Element		Certified Value	Results Obtained Trial 1	Trial 3	Trial 5
Iron	Fe	0.61%	0.60%	0.61%	0.59%
Nickel	Ni	0.57%	0.56%	0.57%	0.57%
Magnesium	Mn	0.37%	0.35%	0.37%	0.36%
Copper	Cu	0.30%	0.30%	0.29%	0.30%
Manganese	Mn	0.26%	0.25%	0.25%	0.26%
Titanium	Ti	0.18%	0.18%	0.19%	0.19%
Zinc	Zn	0.16%	0.17%	0.17%	0.18%
Chromium	Cr	0.11%	0.12%	0.11%	0.12%
Lead	Pb	0.10%	0.10%	0.11%	0.10%
Tin	Sn	0.05%	0.05%	0.05%	0.05%

2. **British Chemical Standards No. 268, Silicon - Aluminum Alloy**

Element		Certified Value	Results Obtained Trial 2	Trial 4
Iron	Fe	0.39%	0.38%	0.40%
Nickel	Ni	0.12%	0.11%	0.12%
Magnesium	Mg	0.56%	0.55%	0.56%
Copper	Cu	1.34%	1.33%	1.32%
Manganese	Mn	0.22%	0.22%	0.21%
Titanium	Ti	L 0.02%	0.015%	0.019%
Zinc	Zn	0.05%	0.056%	0.054%
Tin	Sn	0.03%	0.03%	0.03%

L = Less than